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Effect of Preparation Parameters on Optical Properties of Cu and Ni Doped TiO_2 Photocatalyst

Robabeh Bashiri*,[a], Norani Muti Mohamed[b], Chong Fai Kait[b], Suriati Sufian[a] , Mehboob khatani[b], Hengameh Hanaei[d]

[a]*Chemical Engineering Department,* [b]*Centre of Innovative Nanostructures & Nanodevices (COINN)*
[b]*Electrical & Electronic Engineering Dep, Meechanical Engineering Dep Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar, Perak, Malaysia*

Abstract

A series of bimetallic titania-supported copper-nickel (Cu-Ni/TiO_2) photocatalysts were synthesized using sol–gel associated hydrothermal method coupling with design of experiment (DOE). Central composite design (CCD) was applied to study the single and combined effects of three primary parameters H_2O, acid and Cu ratio to titanium tetraisopropoxide on the optical properties of Cu-Ni/TiO_2. The absorbance of all photocatalysts were extended to the visible region with lower bandgap energies compared to commercial TiO_2 (P25. Analysis of variance (ANOVA) revealed a second–order polynomial regression model to fit the experimental data in CCD. A comparison between predicted and experimental values represented a reasonable agreement amongst them with high coefficient of determination value (R^2=0.94). The 3-D response surface plots imply that parameter water was more effective compared to the other parameters.

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Keywords: Cu-Ni/TiO_2,, bandgap energy, CCD, RSM

1. Introduction

Finding an alternative renewable source of energy is the biggest challenge in the 21st century due to environmental issues. Hydrogen as an energy carrier is a desirable substitute for fossil fuels (1-3). Solar hydrogen production from water and sunlight using photoelectrochemical (PEC) cell is one of the promising methods while the low efficiency of PEC cell is its main limitation.

* Corresponding author. susanbashiri@gmail.com

Honda and Fujishima established photoelectrolysis of water through an n-type semiconductor (TiO_2) as photoanode and harvesting solar energy through the flow of the excited electrons in PEC cell in 1972 (4-6). TiO_2 as a primary semiconductor is a promising photocatalysts due to its unique characteristics like high stability against corrosion, non-toxicity. TiO_2 has wide bandgap energies and absorbance only in the UV region. In order to overcome the limitation of

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PEC cell, TiO_2 photoanode can be modified by doping metal ions. It has been found to be a simple, an inexpensive and effective way to repeatedly prepare modified TiO_2 with enhanced photocatalytic properties (7-9). In recent years, many researchers have focused on bimetallic doped TiO_2 by using transition and noble metal due to their lower Fermi level position compared to TiO_2 which shows apparently higher photocatalytic activity than the single doped TiO_2. The observed improvement is due to the synergistic influence of the second metal on the electronic properties and the formation of active surface structures (10, 11). Sol-gel method associated hydrothermal allows the formation of photocatalysts with crystalline property at low temperature for enhanced photocatalytic performance. Moreover the preparation conditions and parameters of metal doped TiO_2 can impact on the photocatalytic performance (12-14). It is well known that many parameters like water to alkoxide molar ratio, stabilizing agents, solvents, pH and aging time can impact on the photocatalytic activity of TiO_2 in sol-gel method. Design of experiment (DOE) for investigation different parameters is an organized way to find the significant parameter and set up a simultaneous relationship between all of the variables in a set of experiments (15, 16). This paper presents the exploring of influence three different parameters (H_2O/TTIP, acid/TTIP and Cu content) on the optical properties, namely measuring the bandgap energies and the extending of absorbance toward the visible region of Cu-Ni/TiO_2 photocatalysts by applying RSM coupling with central composite design (CCD).

2. Experimental Section

The preparation of the Cu-Ni/TiO2 was followed in our earlier work. The solution I (a mixture of specific amount of titanium tetraisopropoxide (TTIP), ethanol, acetic acid, $Cu(NO_3)_2.3H_2O$ and $Ni(NO_3)_2.6H_2O$) added dropwise under vigorous stirring to solution II (a mixture of water and ethanol). After stirring overnight, the resultant sol suspension was transferred into a Teflon container and placed in a stainless-steel autoclave cell and kept at 180oC for 12 h. The washed samples were dried at 105^{o}C for 12 h and afterward calcined at 450°C for 2 h. DOE was accomplished by using Design-Expert version 8.0.7.1 (Stat-Ease, Inc.) to perform the statistical analysis and construct the regression model. Three numerical factors: water/TTIP (16-80) acid/TTP (1-5) and Cu (5-9) content were investigated (17).

2.1. Characterization

Study the extending absorbance edge to the visible region and bandgap energies are the most important optical property for each photocatalyst. The diffuse reflectance is a standard technique to measure the bandgap energy of powder samples. The diffuse reflectance of incident radiation is considered when the incident light penetrates into the sample and gets reflected by grain boundary of the particles. The bandgap energy was measured by Tauc plot of $[F(R).h\nu]^{1/2}$ vs. hν and line drawn on the liner part where at $[F(R).h\nu]^{1/2}=0$ (18, 19). DRUV-Vis was applied between 200–800nm using carry100 spectrophotometer. Powder samples put in a sample holder to make a smooth layer with thickness 1-3 mm to complete absorbs or scattered all incidents radiant before reaching to the back of the samples.

3. Result and Discussions

3.1. Diffuse–reflectance spectra (DRS)

Figure 1 represents the absorption spectra of the prepared photocatalysts. The absorption edges of all prepared Cu-Ni/TiO2 were shifted into the visible region compared to P25. The absorption peak of TiO_2 into the UV region is generally related to the transition of the excited electrons from the valence band (VB) (O2p state) to the conduction band (CB) (Ti3d state). The absorption in the visible region is a result of the formation the sub-band state of Cu^{2+} and Ni^{2+} in the middle of the bandgap energies to the indirect transition of excited electrons from VB to CB (20). Figure 3 (a, b) illustrates Tauc plot to determine the bandgap energies of the photocatalysts by line drawn on the liner part of F(R) vs. hν plot where at $[F(R).h\nu]^{1/2}=0$. The bandgap energies reduced to less than 3 eV compared to P25 with bandgap energy of 3.2 eV.

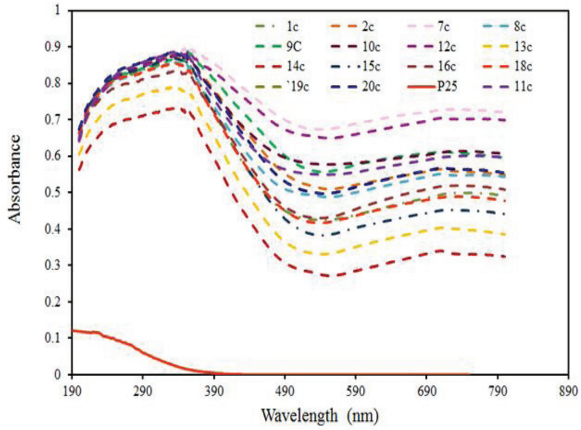

Figure 1: Absorbance spectra of prepared photocatalysts

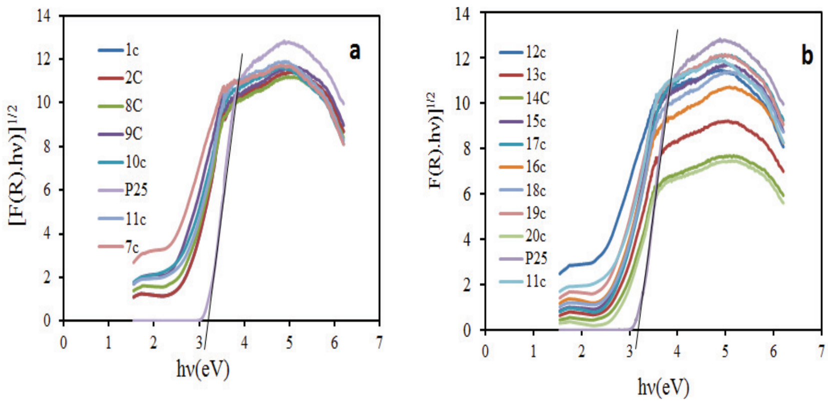

Figure 2: Tauc plots of commercial TiO_2 (p25) and all synthesized photocatalysts (a) runs 1to 11 and b) runs 12to 20

3.2. *Experimental design and analysis of variance (ANOVA)*

The coefficients of the models for the response (bandgap energy) were estimated by multiple regression analysis. The fit quality of the models was judged from their coefficients of correlation and determination. The adequacy of each model was identified by the analysis of variance (ANOVA) using Fisher or F-test. The significance of the equation parameters for response was assessed by p-value (significance probability value) and student-test as suggested by Montgomery (21). The significance test of regression is useful to identify the relationship between the response and a subset of the independent variables. The coded of the quadratic regression model to estimate the coefficients are shown in the Equation 1:

$$\text{Bandgap} = 2.54 + (0.089 \times A) + (-0.017 \times 10^{-3} B) + (-0.044 \times C) + (0.064 \times A \times B) + (-0.096 A \times C) + (0.059 \times B \times C) + (-0.082 \times A^2) + (-0.058 \times B^2) + (0.042 \times C^2) \quad (1)$$

It displays the coded of the first order, second order and interaction between all terms, including A, B, C, AB, AC, BC, A^2, B^2, and C^2. Analysis of variance (ANOVA) for the quadratic model of bandgap energies as the desirable response is shown in Table 1 Fisher's test for ANOVA was applied for statistical testing based on the experimental values. The model shows highly significant results at the 99% confidence level ($P < 0.0001$) and also F-value of 20.21 illustrates that the model is significant and this large value can occur due to noise with chance less 0.01%. The probability of lack of fit F-value (LOF) model is 3.18 and not significant relative to pure error. This large LOF has only 11.49 % chance due to noise and LOF is non-significant which is good to fit the model. The regression model had a high value of the coefficients of determination (R^2= 0.94) for bandgap energies of the photocatalysts. The R^2 value means a good agreement between the experimental and predicted values of the fitted model. It implies that 94 % of the total variation in the response is justified by the model as shown in. Adeq-precision ratio measures the signal to noise ratio, which the ratio greater than 4 is desirable. Therefore, this model with a ratio of 18.322 indicates an adequate signal. The coefficient of variation (CV) is a ratio of the standard error of estimate for the mean value of the observed response, which is a measure of reproducibility of the model. Generally, a model can be considered reasonably reproducible if its CV is not greater than 10 %. Then the CV =2.40 implies a precision and reliability of the experimental runs.

Table 1: Analysis of variance (ANOVA) for the quadratic model of bandgap energies as desirable response

Source	Sum of Squares	[a]Df	Mean Square	F Value	p-value (Prob > F)
Model	0.63	9	0.07	20.21	< 0.0001
A-water	0.13	1	0.13	36.9	0.0001
B-acid	0.004556	1	0.004556	1.32	0.2781
C-Cu	0.032	1	0.032	9.1	0.013
AB	0.033	1	0.033	9.39	0.012
AC	0.074	1	0.074	21.39	0.0009
BC	0.028	1	0.028	7.97	0.0181
A^2	0.17	1	0.17	48.45	< 0.0001
B^2	0.084	1	0.084	24.38	0.0006
C^2	0.044	1	0.044	12.83	0.005
Residual	0.035	10	0.003464		
Lack of Fit	0.026	5	0.005271	3.18	0.1149
Pure Error	0.008283	5	0.001657		
[b]Std.Dev.=0.059		R^2=0.9479		Adj-R^2=0.9018	[c]C.V.% = 2.40

It is notable that the model terms with p-value between 0.05 and 0.1 are significant and the term with small magnitude of the p-value has greater significance and contributes largely towards the response variable. The analysis data from Table 1 demonstrates that the first and second order of all terms except for the first order of term B (acid to TTIP ratio) was significant. Moreover the two-level interaction between all terms were significant. The p-values of regression model: A (H_2O/TTIP) and C (Cu content) are 0.001 and 0.013, respectively. Therefore H_2O/TTIP has the highest effect to the response (bandgap energies) followed by Cu content, A > C> B. The data can accurately fit the model and it can be used for the prediction of the variables within the given range. Finally, fitting the model can be carried precisely by data and this model is a considerable model to predict the variables within the given ranges. Figure 3 displays the plotted actual (observed) value versus predicted value of the bandgap energies with tendencies in the linear regression fit.

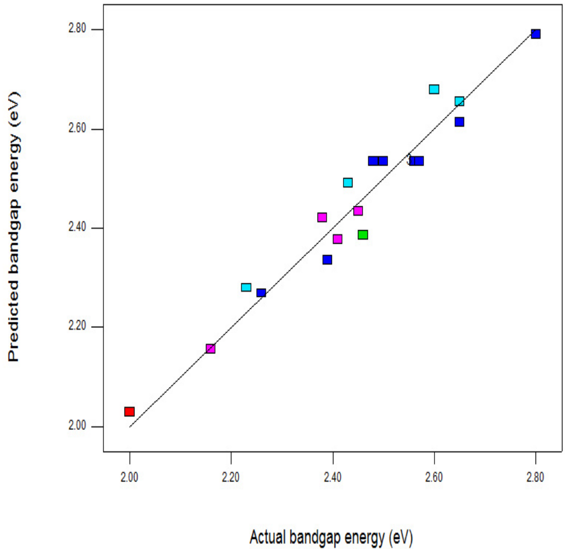

Figure 3: Relation between experimental and predicted bandgap energies using Eq.1

Figure 4 (a) illustrates the 3-D response surface plot and the contour plot of the bandgap energies with varying water and acid to TTIP molar ratio by holding the Cu content at the center point (C=7). The bandgap energies were decreased by reducing the amount of H_2O/TTIP molar ratio from 80 to 16. Increasing the acid/TTIP molar ratio of 1 to 3 has the positive effect on the bandgap energies while increasing the acid/TTIP has the negative effect on the bandgap energies. The counter plots and 3D graph depict that the effect of term A on the bandgap energies is more compared to term B as shown earlier due to higher P-value. Furthermore the effect of second order terms A and B is clearly obvious. The 3-D response surface and its respective contour plots of the interaction between H_2O/TTIP and Cu content at the center point of acid /TTIP are displayed in Figure 4 (b). The influence of parameter A has the same trend for bandgap energies as explained earlier with less influence of second order terms. The Cu amount has the negative effect on the bandgap energy and it sharply dropped from 9 to 6.5 mol% while the bandgap energies slightly went up with reducing Cu amount to less than 6 mol%. It notable that the linear effect of Cu content on the bandgap energy is lowers than H_2O/TTIP molar ratio due to fewer coefficients and the second effect of term C is not obviously clear compared with term A due to lower P- value and less significant. In addition, the effect of interaction between A and C is less significant on the bandgap energies compared to AB. Figure 4(c) shows that terms B is more effective compared to C. The bandgap energies gradually rise by increasing the acid/TTIP from 1 to 3 molar ratio and adding more acid reduced the bandgap energies which is suitable for photocatalytic performance. When Cu content was reduced from 5 to 7 mol%, the bandgap energies dropped and adding more Cu content slightly increased the bandgap energies. The effect of the interaction of B and C was less significant compared to AC. A set of solutions that were given by the software in order to identify the optimum conditions of bandgap energies. The best assumed condition (A:16, B:3 and C:7) applicable in actual operating condition to obtain the minimum bandgap energy 2 eV, which it can be used to increase the photocatalytic performance of Cu-Ni/TiO_2 as photoanode in the photoelectrochemical cell.

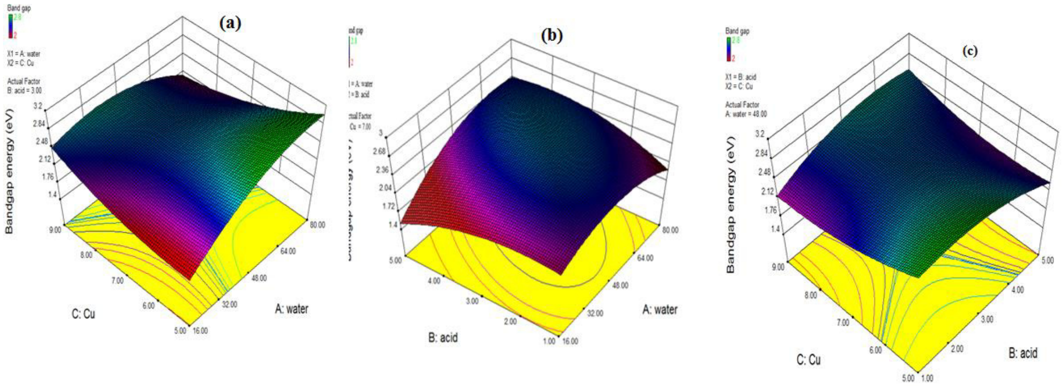

Figure 4: Response surface 3D and counter plot effect of interaction between (a) water /TTIP molar ratio Cu content, (b) water /TTIP and acid/TTIP molar ratio and (c) acid /TTIP molar ratio Cu content

4. Conclusion

The bimetallic Cu-Ni/TiO_2 photocatalysts were synthesized successfully using sol-gel hydrothermal method. The effects of three independent variables: water/ TTIP (A) and acid /TTIP molar ratio (B) and Cu content (C) were investigated using RSM coupling CCD. A second–order polynomial regression model was used to fit the experimental data in CCD. The ANOVA analysis exposed that all terms and their interaction are significant except B. This model was fitted with R^2 =94 %. A set of optimum conditions was suggested by the software to achieve bandgap energy around 2.0 eV. Decreasing the bandgap energy extended the absorption to visible region as the same direction with our objective. This study makes available, reproducible routes for controlling the bandgap energies of Cu-Ni/TiO_2 for hydrogen production application and optimization the photoconversion processes to improve the efficiency in the photoelectrochemical cell.

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